19. *An Infra-red Spectroscopic Investigation of the Reaction between Acetic Anhydride and Butyric Anhydride.*

By L. Brown and I. F. Trotter.

Spectroscopic evidence has been obtained for the existence of acetic butyric anhydride and the results show it to be in equilibrium with the two simple anhydrides. The equilibrium constant shows no detectable variation over the temperature range 20—100°, and consequently the heat of reaction must be very small and the equilibrium is determined by the entropy change which takes place. This must be attributed almost entirely to the change in the relative external symmetry numbers and this leads to a value of 4 for the equilibrium constant, a value giving consistent results for the extinction coefficients of the mixed anhydride. The rate of reaction is such that it can be conveniently followed spectroscopically over the temperature range 25—45°, and measurements on the velocity constant at three temperatures gave a value of about 10 kcals. for the energy of activation.

Interest in the mixed anhydrides was revived when in 1932 it was shown that keten would react with acetic acid to give acetic anhydride, and it was claimed that it would react with other carboxylic acids to give mixed anhydrides which were stated to be unstable to heat (Hurd and Dull, *J. Amer. Chem. Soc.*, 1932, **54**, 3427). Work on the mixed anhydrides has, however, been hampered because of the lack of any quantitative method for their analysis, an equimolecular mixture of two simple anhydrides being indistinguishable by chemical analysis from the corresponding mixed anhydride.

In an attempt to develop a spectroscopic method for the analysis of the system acetic acid–acetic anhydride–butyric acid–butyric anhydride, it was found that the spectra of mixtures of these various components varied with time. For example, if the spectrum of a mixture of acetic acid and butyric anhydride was measured immediately after preparation, it was found to be the additive sum of those of the primary constituents. If, however, the mixture was allowed to stand for some time before measurement of the spectrum, bands were observed which were characteristic of acetic anhydride and butyric acid together with certain additional bands which were not attributable to any of these four components. These additional bands were also observed in the spectra of mixtures of acetic anhydride and butyric acid and in mixtures of the two simple anhydrides, provided that in each case the solutions had been left for some time before the spectra were measured. These additional bands must be caused by formation of a mixed acetic butyric anhydride, and could in consequence be used for its detection and determination. Of these various reactions the simplest for spectroscopic study is that between the two simple anhydrides, as this gives rise to a three-component system as opposed to the five-component system obtained if a carboxylic acid is used as one of the primary components.

Experimental.

The samples used for the study of the reactions were the following : (*a*) Acetic anhydride obtained by treatment with sodium of a commercially pure sample, followed by fractionation from a mixture of sodium and sodium acetate; the final fraction was spectroscopically free from acetic acid. (*b*) Butyric anhydride prepared by fractionation of a commercially pure sample; the final fraction was spectroscopically free from butyric acid. (*c*) Carbon tetrachloride obtained by washing a commercial sample with sodium hydroxide solution, then with water, and drying (Na_2SO_4) and fractionating it; the product was transparent to radiation at 3 μ. in a 2-cm. absorption cell.

The spectra were measured on a Hilger D.209 spectrometer fitted with a sodium chloride prism and used as a single-beam photographic recorder.

All the spectra were measured in a sealed absorption cell, about 0·1 mm. thick, similar to that described by Colthup (*Rev. Sci. Instr.*, 1947, **18**, 64). Liquid was introduced into the cell through one of two stainless-steel tubes, and could be removed by inserting the two tubes into two pieces of pressure tubing, one connected through a drying tube to the atmosphere and the other to a vacuum line. Provision was also made for flushing the cell with a stream of carbon tetrachloride.

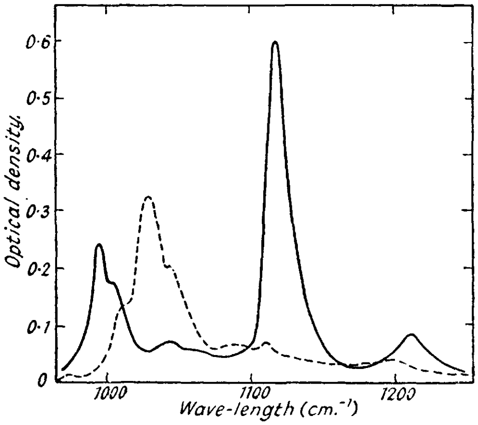
In making quantitative measurements, a trace was taken of the sample followed immediately by one of the solvent on the same wave-length scale. This method of superimposing the background was justified by the results obtained. The effect of scattered radiation was minimized by using a glass scatter shutter.

In following the rates of reaction, the reaction vessel was placed in a constant-temperature bath and continuously agitated by an eccentric drive taken from the stirrer motor.

RESULTS AND DISCUSSION.

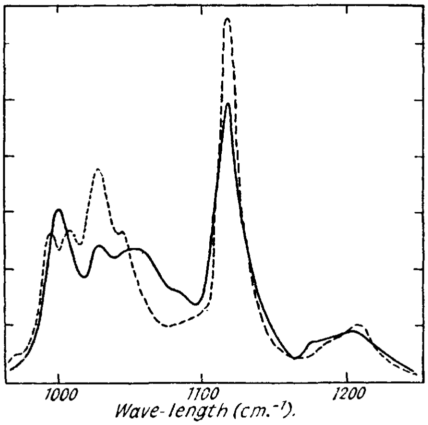
(*a*) *Choice of Characteristic Frequencies.*—The spectra of solutions of acetic anhydride and butyric anhydride in carbon tetrachloride solution are shown in Fig. 1 over the range 950—1250 cm.$^{-1}$. In Fig. 2 the broken line represents the spectrum of a mixture of the two anhydrides at the same concentrations as in Fig. 1 on the assumption that no interaction takes place, and the full line represents the observed spectrum after equilibrium is reached. Of the new bands which appear, the strongest is at 1000 cm.$^{-1}$, and its appearance is accompanied by a decrease in the intensities of the butyric anhydride and acetic anhydride bands at 1029 and 1125 cm.$^{-1}$, respectively. These three bands occur in a relatively narrow region of the spectrum which can conveniently be covered at one setting of the spectrometer slits (0·025 cm.), and moreover, carbon tetrachloride has very little absorption in this region. Thus the most convenient choice of key frequencies is as follows :

FIG. 1.



——— *Acetic anhydride.*
– – – – *Butyric anhydride.*

FIG. 2.
Mixture of acetic and butyric anhydrides.



——— *At equilibrium*
– – – – *At time* = 0.

Acetic butyric anhydride	1000 cm.$^{-1}$ (ν_1)
Butyric anhydride	1029 cm.$^{-1}$ (ν_2)
Acetic anhydride	1125 cm.$^{-1}$ (ν_3)

In order to analyse mixtures of these three components, it is necessary to know the extinction coefficients of each component at each of the three key frequencies. For the two simple anhydrides this presents no difficulty, but, as from the nature of the reaction the mixed anhydride cannot be isolated, it is necessary to obtain the extinction coefficients of acetic butyric anhydride indirectly.

(*b*) *Measurement of the Extinction Coefficients of Acetic and Butyric Anhydrides at* ν_1, ν_2, *and* ν_3.—Solutions of acetic and butyric anhydrides were made up in carbon tetrachloride at a series of concentrations, and the measured optical densities at ν_1, ν_2, and ν_3 plotted against concentration. In each case straight lines were obtained which passed through the origin, showing that over the concentration range studied the solutions obeyed Beer's law, which may be written in the form $D_\nu = -\log_{10} T_\nu = \alpha_\nu cd$, where D_ν is the optical density and T_ν the transmission at frequency ν, c is the concentration of the component, d the cell thickness, and

α_ν the extinction coefficient. It is convenient to compound the cell thickness and the extinction coefficient to give ε_ν, the apparent extinction coefficient, which may be defined by the equation $D_\nu = \varepsilon_\nu c$.

The units chosen to express the concentration were g. per 50 ml. of solution. Then, if ε_{ij} is the extinction coefficient defined in this way for the ith component at the jth frequency, the results obtained for the two simple anhydrides may be summarized as follows :

$$\varepsilon_{21} = 0{\cdot}089;\ \varepsilon_{22} = 0{\cdot}660;\ \varepsilon_{23} = 0{\cdot}105;\ \varepsilon_{31} = 0{\cdot}350;\ \varepsilon_{32} = 0{\cdot}058;\ \varepsilon_{33} = 1{\cdot}363$$

As it was intended to measure the rate of the reaction at a series of temperatures, it was necessary to see if any consistent error was introduced if the solutions were measured at temperatures more than a few degrees removed from room temperatures : it was found that no such error was introduced over the temperature range used.

(*c*) *Variation of Equilibrium Constant with Temperature.*—Standard solutions of acetic and butyric anhydrides were prepared at room temperature, then brought to the appropriate temperature, mixed in various proportions, and allowed to come to equilibrium. In order to carry out measurements at 100°, the reaction was carried out in a sealed tube, and the equilibrium subsequently frozen in solid carbon dioxide–acetone. The measured mean equilibrium values of the optical density for a series of experiments are listed in Table I, each being the mean of at least six measurements. The initial concentrations of butyric anhydride, C_2°, and acetic anhydride, C_3°, are in g./50 ml.

TABLE I.

Expt.	Temp.	C_2°.	C_3°.	D_1.	D_2.	D_3.	Expt.	Temp.	C_2°.	C_3°.	D_1.	D_2.	D_3.
A	25°	0·538	0·647	0·395	0·253	0·712	D	25°	0·808	0·431	0·358	0·423	0·463
B	35	0·538	0·647	0·401	0·257	0·723	E	35	0·808	0·431	0·355	0·421	0·463
C	45	0·538	0·647	0·395	0·256	0·706	F	45	0·808	0·431	0·351	0·430	0·457
G	19·7	0·650	0·682	0·444	0·299	0·760	I	19·7	0·871	0·439	0·360	0·445	0·476
H	100	0·650	0·682	0·440	0·304	0·760	J	100	0·871	0·439	0·365	0·441	0·477

From these results it follows that within the limits of experimental error the equilibrium constant is independent of temperature over the range 20—100°, and this is evident without any knowledge of the extinction coefficients of the mixed anhydride. The thermodynamic implications of this result are that the overall heat of reaction is zero, that there is no change in internal energy, and that the equilibrium constant is determined solely by the entropy change. In this respect the reaction is evidently analogous to certain processes of ester exchange (Calingaert *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 2748), to the redistribution of metal alkyls (*idem, ibid.*, p. 2755; 1940, **62**, 1104, 1107, 1542; 1941, **63**, 94), and to the redistribution of halogen that takes place between the glycol dihalides (*idem, ibid.*, 1940, **62**, 1545).

The change in entropy (ΔS°) for this type of reaction should be measured by the relative external symmetry numbers σ of the molecules involved in the equilibrium; the only other appreciable contributions to ΔS° would lie in the effect of the redistribution of mass on the translational entropies and in the redistribution of the principal moments of inertia on the rotational entropies. These contributions are likely to be small, so that the controlling factor in the equilibrium in the case where the heat content change is zero would be expected to be $(\Delta S^\circ)\sigma$. For the reaction in question the relative external symmetry numbers are 2 for the simple anhydrides and unity for the mixed anhydride, which leads to a value of 4 for the equilibrium constant when the concentrations are expressed in moles per unit volume.

(*d*) *Calculation of Extinction Coefficients of the Mixed Anhydride.*—It is not necessary to know the value of the equilibrium constant to evaluate the extinction coefficients of the mixed anhydride, but without this knowledge the overall accuracy of the calculation is low and the best results are obtained by using the value of the equilibrium constant derived above. Suppose C_1, C_2, and C_3 are the equilibrium concentrations of acetic butyric, butyric, and acetic anhydrides in g. per unit volume, and M_1, M_2, and M_3 are the respective molecular weights. Then,

$$C_1^2/C_2C_3 = 4M_1^2/M_2M_3 = 4{\cdot}190 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

The equilibrium concentrations will be related to the initial concentrations of the two simple anhydrides by the equations

$$C_1/260 = (C_2^\circ - C_2)/158 = (C_3^\circ - C_3)/102$$

whence

$$C_2 = C_2^\circ - 0{\cdot}608C_1 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

and

$$C_3 = C_3^\circ - 0{\cdot}392C_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Substitution for C_2 and C_3 in equation (1) gives

$$C_1 = 4{\cdot}190C_2^\circ C_3^\circ/(2{\cdot}550C_3^\circ + 1{\cdot}643C_2^\circ) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence, by using equations (2), (3), and (4) it is possible to derive C_1, C_2, and C_3 from the initial concentrations.

The optical densities at ν_1, ν_2, and ν_3 are related to the unknown extinction coefficients by the equations

$$\left.\begin{aligned} D_1 &= \varepsilon_{11}C_1 + 0{\cdot}089C_2 + 0{\cdot}350C_3 \\ D_2 &= \varepsilon_{12}C_1 + 0{\cdot}660C_2 + 0{\cdot}058C_3 \\ D_3 &= \varepsilon_{13}C_1 + 0{\cdot}108C_2 + 1{\cdot}363C_3 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Hence from equation (5) it is possible to evaluate ε_{11}, ε_{12}, and ε_{13} from the calculated concentrations C_1, C_2, and C_3 and from the measured equilibrium optical densities. The results of these calculations are given in Table II.

TABLE II.

Expt.	C_2°.	C_3°.	D_1.	D_2.	D_3.	ε_{11}.	ε_{12}.	ε_{13}.
I, IV, VII	0·674	0·540	0·375	0·326	0·585	0·396	0·179	0·236
II, V	0·898	0·361	0·322	0·465	0·380	0·397	0·184	0·231
III	0·448	0·695	0·395	0·208	0·808	0·405	0·181	0·240
A, B, C	0·538	0·647	0·397	0·255	0·714	0·404	0·186	0·208
D, E, F	0·808	0·431	0·355	0·425	0·461	0·411	0·206	0·243
G, H	0·650	0·682	0·442	0·302	0·760	0·411	0·172	0·239
I, J	0·871	0·439	0·362	0·443	0·476	0·400	0·174	0·255
VI	0·337	0·539	0·303	0·161	0·624	0·406	0·190	0·228
VIII	0·561	0·449	0·318	0·275	0·494	0·409	0·188	0·249
IX	0·481	0·385	0·270	0·234	0·422	0·406	0·175	0·251
					Mean	0·404	0·184	0·236

By substituting these values for the extinction coefficients in equation (5) and solving for the concentration terms, the equations

$$\left.\begin{aligned} C_1 &= 3{\cdot}106D_1 - 0{\cdot}290D_2 - 0{\cdot}785D_3 \\ C_2 &= -0{\cdot}829D_1 + 1{\cdot}618D_2 + 0{\cdot}144D_3 \\ C_3 &= -0{\cdot}500D_1 - 0{\cdot}078D_2 + 0{\cdot}865D_3 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

are obtained, from which C_1, C_2, and C_3 may be obtained directly in terms of D_1, D_2, and D_3.

The constancy of the values of the extinction coefficients derived from the various experiments (Table II) provides confirmation of the value of the equilibrium constant deduced from the observation that the equilibrium optical densities were independent of temperature.

(*e*) *Determination of the Energy of Activation of the Reaction.*—It was found that the reaction proceeded at a conveniently measurable rate over the temperature range 25—45°. At 25° it was sufficiently slow to enable the spectrum to be measured over all three characteristic frequencies, but at 35° and 45° the time between successive measurements had to be cut to a minimum and it was found convenient to follow the reaction by measuring D_3 alone until equilibrium was reached, whereupon the optical densities at all three frequencies were measured. Thus at 25° (Runs I—III) measurements were made at intervals of 9—10 minutes, whereas at 35° and 45° the time interval was reduced to 3·5—4·5 minutes (Runs IV—IX).

For a reaction of the type $\mathrm{A} + \mathrm{B} \rightleftharpoons 2\mathrm{C}$, if the initial concentrations of A, B, and C are *a*, *b*, and 0 moles per unit volume, if after time *t* the concentration of C is $2x$ moles per unit volume, and if the equilibrium constant is 4, then the velocity constant of the forward reaction (*k*) is given by the expression

$$k = \frac{-2}{t} \cdot \frac{1}{a+b} \ln\left(1 - \frac{a+b}{ab}x\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For the reaction between butyric and acetic anhydrides: $a = C_2^\circ/158$; $b = C_3^\circ/102$, and $2x = C_1^t/130$, whence

$$k = \frac{-1}{t} \cdot \frac{728}{C_2^\circ + 1{\cdot}549C_3^\circ} \log_{10}\left(1 - \frac{C_2^\circ + 1{\cdot}549C_3^\circ}{C_2^\circ C_3^\circ} \cdot \frac{C_1^t}{2{\cdot}55}\right) \quad . \quad . \quad . \quad (8)$$

Direct substitution in equation (8) will give k in units of 50 ml. mole^{-1} min.$^{-1}$.

If D_j^0 is the initial optical density at the jth frequency and D_j^t is the optical density at time t, then

$$D_j^t = \varepsilon_{1j}C_1^t + \varepsilon_{2j}C_2^t + \varepsilon_{3j}C_3^t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Eliminating C_2^t and C_3^t by means of equations (2) and (3) and writing the change in optical density between times t and 0 as ΔD_j^t, we have

$$\Delta D_j^t = (\varepsilon_{1j} - 0{\cdot}608\varepsilon_{2j} - 0{\cdot}392\varepsilon_{3j})C_1^t \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

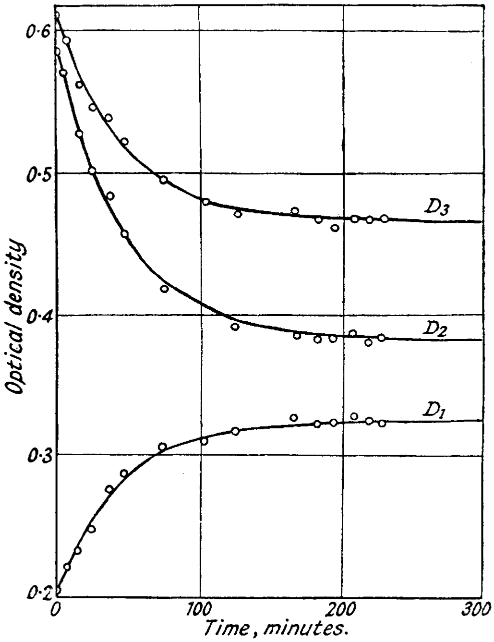
Insertion of the experimental values of the extinction coefficients in equation (10) gives

$$\Delta D_1^t = 0{\cdot}214C_1^t; \quad \Delta D_2^t = -0{\cdot}240C_1^t; \quad \Delta D_3^t = -0{\cdot}364C_1^t \quad . \quad . \quad . \quad (11)$$

From equation (11) it follows that, knowing the equilibrium values of ΔD_1, ΔD_2, and ΔD_3, it is possible to calculate any two of the optical densities at time t if the third is known. Conversely, if all three optical densities are known, it is possible to use equation (11) to average the three sets of results. This was done for runs I, II, and III, so that all three rate curves could be averaged to give a mean value for the velocity constant.

FIG. 3.

Run II. Reaction at 25°.



In Fig. 3 is shown the variation of optical density with time for the three key frequencies in run II, the reaction being measured at 25°. Runs I, IV, and VII started with the same initial concentrations but were carried out at 25°, 35°, and 45°, respectively, and the rate curves (D_3 versus t) for these runs are illustrated in Fig. 4. The velocity constants were obtained by measuring D_3 at various times from the rate curves, obtaining C_1^t from equation (11), and substituting the value so obtained together with the values of C_2^0 and C_3^0 in equation (8), the mean value of k for each curve being taken. The results obtained for the velocity constants are given in Table III.

For each set of runs at a given temperature, the mean variation in the velocity constant is about ±14%. This could be accounted for by the errors introduced in drawing the rate curves, but there is a further source of error, namely, the possibility of absorption of a certain amount of water during the preparation of the solutions. It was found during the preliminary measurements that reactions of the following type can take place: AcOH + Ac′OAc′ $\rightleftharpoons$ AcOAc′ + Ac′OH, where Ac and Ac′ are two acyl radicals.

Reactions of this type have been known for some time, and it is thus possible that the reaction between the two anhydrides is catalysed by acid. Although the anhydrides and the carbon tetrachloride were carefully purified before use, it is difficult to obtain an anhydride completely free from acid, and as anhydrides are hygroscopic, a certain amount of water could be taken up during the preparation of the solutions and during sampling. If the amount so taken up were to vary from run to run it might introduce a variation in the velocity constant.

TABLE III.

Run.	Temp., °K.	k, 50 ml. mole^{-1} min.$^{-1}$.	k (mean), l. mole^{-1} min.$^{-1}$.
I	298	3·25	0·196
II	298	4·77	
III	298	3·71	
I, II, III	298	3·91	
IV	308	5·31	0·336
V	308	7·83	
VI	308	7·01	
IV, V, VI	308	6·72	
VII	318	10·50	0·595
VIII	318	10·90	
IX	318	14·30	
VII, VIII, IX	318	11·90	

In Fig. 5 is shown a graph of $-\ln k$ against $1/T$, and from the slope of the line the energy of activation is 10,600 cals. In view of the variation in k between one run and another and the, small temperature intervals available for study, the energy of activation may be taken as being of the order of 10 kcals.

FIG. 4.

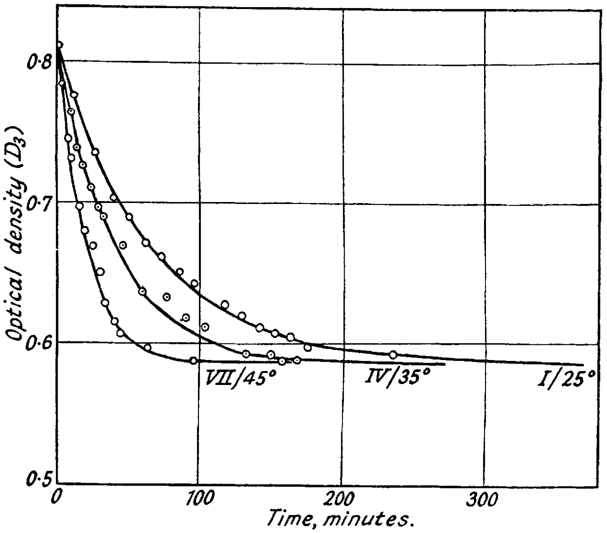
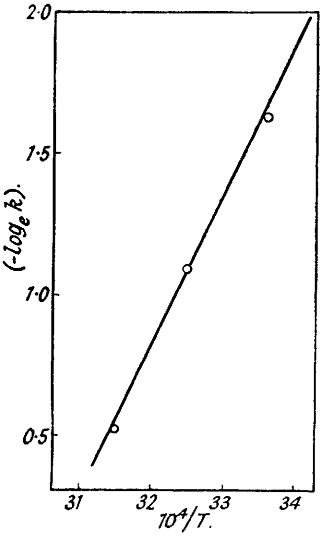


FIG. 5.



E = 10,600 *cals.* (*from slope of line*).

The observation that acetic butyric anhydride exists in equilibrium with the two simple anhydrides is of interest in connection with the work of Verkade (*Rec. Trav. chim.*, 1916, **35**, 299) and of Kilpatrick and Kilpatrick (*J. Amer. Chem. Soc.*, 1930, **52**, 1418) on acetic propionic anhydride. They found that the hydrolysis of the mixed anhydride proceeded as a first-order reaction with a reaction velocity intermediate between the values for the symmetrical anhydrides, and interpreted this result as showing that they were dealing with a true mixed anhydride and not with a mixture of the two simple anhydrides. If the rate of disproportionation of acetic propionic anhydride is comparable with that of acetic butyric anhydride, then at the temperature at which the rate of hydrolysis was measured, 0°, the rate of disproportionation would be very slow compared with the rate of hydrolysis, so that the disproportionation reaction could be neglected.

It is noteworthy that, once the equilibrium constant for the reaction between the two anhydrides is known, the extension of the analytical method to include the components acetic acid and butyric acid is relatively simple. The characteristic frequencies chosen for butyric acid and acetic acid were 1220 cm.$^{-1}$ (ν_4) and 1288 cm.$^{-1}$ (ν_5), respectively, and the optical densities at the five key frequencies are related to the concentrations of the components by the equations

$$\begin{aligned}
D_1 &= 0{\cdot}405C_1 + 0{\cdot}089C_2 + 0{\cdot}350C_3 + 0{\cdot}021C_4 + 0{\cdot}041C_5\\
D_2 &= 0{\cdot}184C_1 + 0{\cdot}660C_2 + 0{\cdot}058C_3 + 0{\cdot}053C_4 + 0{\cdot}034C_5\\
D_3 &= 0{\cdot}236C_1 + 0{\cdot}108C_2 + 1{\cdot}363C_3 + 0{\cdot}021C_4 + 0{\cdot}009C_5\\
D_4 &= 0{\cdot}093C_1 + 0{\cdot}028C_2 + 0{\cdot}171C_3 + 0{\cdot}184C_4 + 0{\cdot}026C_5\\
D_5 &= 0{\cdot}043C_1 + 0{\cdot}043C_2 + 0{\cdot}011C_3 + 0{\cdot}195C_4 + 0{\cdot}880C_5
\end{aligned}$$

Solving for the concentration terms, we have

$$\begin{aligned}
C_1 &= +3{\cdot}099D_1 - 0{\cdot}284D_2 - 0{\cdot}776D_3 - 0{\cdot}052D_4 - 0{\cdot}124D_5\\
C_2 &= -0{\cdot}751D_1 + 1{\cdot}606D_2 + 0{\cdot}172D_3 - 0{\cdot}378D_4 - 0{\cdot}018D_5\\
C_3 &= -0{\cdot}464D_1 - 0{\cdot}074D_2 + 0{\cdot}861D_3 - 0{\cdot}042D_4 + 0{\cdot}017D_5\\
C_4 &= -1{\cdot}039D_1 - 0{\cdot}024D_2 - 0{\cdot}451D_3 + 5{\cdot}732D_4 - 0{\cdot}166D_5\\
C_5 &= +0{\cdot}121D_1 - 0{\cdot}058D_2 + 0{\cdot}119D_3 - 1{\cdot}249D_4 + 1{\cdot}169D_5
\end{aligned}$$

The results serve to show the applicability of the spectroscopic method to the study of chemical reactions, in particular to those in which no chemical analysis of the system is possible.

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